

Distribution of NMR relaxations in a random Heisenberg chain

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Nuclear magnetic resonance (NMR) measurements of the ^{29}Si spin-lattice relaxation time T_1 were used to probe the spin- $1/2$ random Heisenberg chain compound $\text{BaCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_7$. Remarkable differences between the pure ($x = 0$) and the fully random ($x = 0.5$) case are observed, indicating that randomness generates a distribution of local magnetic relaxations. This distribution, which is reflected in a stretched exponential NMR relaxation, exhibits a progressive broadening with decreasing temperature, caused by a growing inequivalence of magnetic sites. Compelling independent evidence for the influence of randomness is also obtained from magnetization data and Monte Carlo calculations. These results suggest the formation of random-singlet states in this class of materials, as previously predicted by theory.

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Random variations of the exchange coupling constant J in ferro- and antiferromagnetic systems (bond randomness) can have a profound effect on their magnetic properties. An innovative scheme for studying random spin- $1/2$ Heisenberg chains (RHCs) was developed already in 1979 by Dasgupta and Ma [1]. Their real-space renormalization group (RSRG) method was extended by Fisher [2], and later employed for a much larger variety of problems related to quenched disorder in quantum magnets. Among these are chains with random ferro- and antiferromagnetic couplings [3], disordered spin-1 chains and spin- $1/2$ ladders [4, 5], Heisenberg magnets in two and three dimensions [6], as well as dilute spins in doped semiconductors [7]. At the core of the RSRG method is the so-called decimation procedure. For RHCs it involves an iterative suppression of the degrees of freedom of the most strongly coupled spins via the formation of “frozen” singlets. Fisher [2] has shown that this procedure converges to a *universal* fixed point. The resulting ground state, characterized by spins coupled at all possible distances and energy scales, is also known as the *random singlet* (RS) state. At low temperatures, only excitations of the most weakly bound singlets are expected to be relevant [8]. As a result, regardless of the microscopic details of the disorder, a large class of bond-disordered systems share universal low-temperature and low-energy properties. In recent years, besides providing predictions for bulk properties, new theoretical work has started to address also the problem of dynamical observables [8, 9].

To date only a few good realizations of RHCs have been achieved. Some early examples [10] were later found to have additional intricacies beyond the Heisenberg chain model [11]. Usually RHCs are obtained as solid solutions of two prototypical spin-chain compounds with different physical properties. A well known example is $\text{Sr}_3\text{CuPt}_{1-x}\text{Ir}_x\text{O}_6$ [12], whose bulk properties are in agreement with the RSRG predictions. To obtain a

direct *microscopic* insight on the problem, we employed NMR experiments to study the local magnetic relaxations in a similar system, namely $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ [13]. In this Letter we show that a strongly temperature-dependent distribution of magnetically inequivalent local relaxations indeed exists in an RHC material. In the context of the above-mentioned decimation procedure, we regard this phenomenon as an indication of the formation of an RS state.

The material $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ considered here, is isostructural with its parent Si- and Ge- compounds. The quasi-1D system $\text{BaCu}_2\text{Si}_2\text{O}_7$ (see Fig. 1) has an in-chain coupling $J = 24.1$ meV [14] and orders antiferromagnetically at $T_N = 9.2$ K [15]. Bond randomness in $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ is introduced via the different bond angles of Cu-O exchange paths, a direct consequence of the different Si and Ge covalent radii. A previous study [16] revealed a logarithmic temperature dependence of the spin susceptibility $\chi(T)$ at low temperatures [1], a characteristic RHC feature predicted to be *independent* of the initial J distribution. Despite that, and following some original misinterpretation, inelastic neutron scattering experiments were found to be quantitatively consistent with Luttinger-liquid behavior expected for a disorder-free spin chain with a single effective coupling $J_{\text{eff}} = (J_{\text{Si}} + J_{\text{Ge}})/2 \approx 37$ meV [16, 17]. It was concluded that the RS-related physics manifests itself at energies much lower than those accessed by neutron studies. Probing these lower-energy/longer-time scales with NMR was the main motivation of the present work.

High-quality single crystals of $\text{BaCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_7$ with $x = 0$ and $x = 0.5$ were grown by the floating zone technique. The magnetic susceptibility was measured via dc SQUID magnetometry. Spin-lattice relaxation times T_1 were measured using standard pulse techniques. Due to the rather long relaxation times (tens of seconds at low temperatures), an aperiodic saturation recovery with an

echo detection was chosen. With a field $\mu_0 H = 7.024$ T applied along the a -axis, the ^{29}Si NMR signal was found at 59.414 MHz.

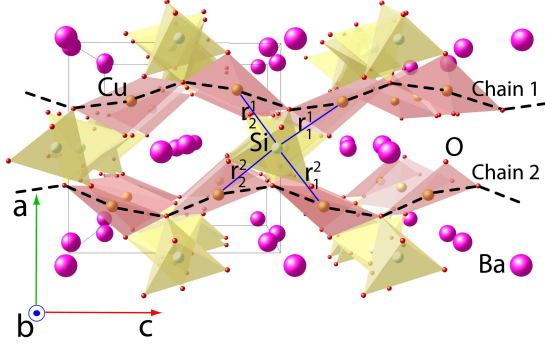


FIG. 1. (Color online) Crystal structure of $\text{BaCu}_2\text{Si}_2\text{O}_7$ emphasizing the copper chains (dashed lines) and the NN configuration of the silicon atoms.

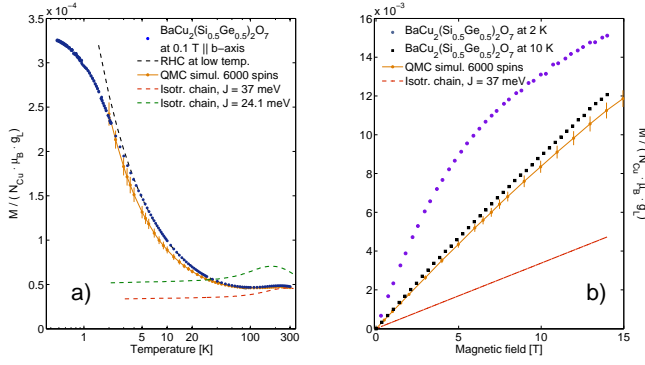


FIG. 2. (Color online) Magnetization M per Cu ion of $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ as a function of temperature (a), and field (b), normalized with respect to the saturation moment, assuming $g_L = 2$. The fit of $M(T)$ with an RHC model was adopted from Ref. 2, while the $M(T)$ and $M(H)$ curves for chains with a single isotropic exchange value were calculated as in Ref. 18. QMC simulations of RHCs are also shown (see text). The symbols are explained in the panels.

That it is precisely the low-energy dynamics of $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ which is most affected by randomness has a clear confirmation in the measured bulk magnetic response (Fig. 2). Unlike for disorder-free spin chains (light dashed lines), the magnetization $M(T)$ of the disordered material (dots) tends to diverge at low temperatures. This divergence is notably different from that observed for $x = 1$, where it is related to weak ferromagnetism and thus strongly orientation-dependent [19]. In our case, instead, the $M(T)$ curves only reflect the weak anisotropy of the g -factor tensor. We interpret the $x = 0.5$, low- T magnetization by the RS theory, which attributes it to the low-energy states associated with the above-mentioned weakly-bound singlets. It predicts $\chi(T) \sim T^{-1} \ln^{-2}(\Omega/T)$ [2], providing a good fit

to the data above 4 K with a cutoff $\Omega \simeq 66.3 \pm 0.7$ meV (dark dashed line). Since the iterative decimation procedure suppresses the strongly bound singlets with an effective coupling larger than T , the fraction of unpaired spins is $n_T \sim 1/[\ln(\Omega/T)]^2$. The paramagnetism of this fraction implies $\chi(T) \sim n_T/T$, with Ω the temperature above which the entire chain is effectively in a paramagnetic regime. The characteristic energy scale of the disorder-induced excitations is, however, much lower than Ω , because already a 5 T magnetic field seems to saturate them. This is clearly evidenced by the slope of $M(H, 2\text{ K})$, which at higher fields tends to that of a disorder-free chain (Fig. 2b). Quantum Monte Carlo (QMC) simulations of Heisenberg spin-1/2 chains, using 6000 spin sites with randomly distributed but equally probable J_{Si} and J_{Ge} couplings, confirm these results. $M(T)$ and $M(H)$ averaged over many ($N > 40$) random configurations were obtained via a directed-loop algorithm [20] within the ALPS 2.0 package [21] and are shown in Fig. 2. The $M(H)$ comparison is made at 10 K, where the system can be treated as 1D. Considering the lack of any free parameters, the agreement with data is remarkably good. Incidentally, a fit of the RS prediction to the low- T QMC results provides $\Omega \approx J_{\text{Ge}}$, thus reinforcing the pertinence of the RS theory.

Similarly to the magnetization data, also ^{29}Si NMR relaxation rates T_1^{-1} for $x = 0$ and $x = 0.5$ show remarkable differences (see Fig. 3). The local magnetic field at the silicon nuclei originates from the Cu electronic spins \mathbf{S}_j and the relevant hyperfine interactions (see Fig. 1). Provided a matrix description of the latter is adequate and the hyperfine coupling tensor at the j -site for the c -chain is $A^{j,c}$ (see Fig. 1 for the index notation), the q -space quantities $\tilde{A}_{\alpha,\beta}^c(\mathbf{q}) = \sum_{j=1,2} e^{i\mathbf{q} \cdot \mathbf{r}_j^c} A_{\alpha,\beta}^{j,c}$, with $\alpha, \beta = \{x, y, z\}$ determine the longitudinal relaxation rate:

$$\frac{1}{T_{1z}} \propto \hbar^2 k_B T \gamma_n^2 \sum_{\alpha=x,y,z} \left[\tilde{A}_{x\alpha}^2(\mathbf{q}) + \tilde{A}_{y\alpha}^2(\mathbf{q}) \right] \frac{\chi''_{\alpha\alpha}(\mathbf{q}, \omega_n)}{\omega_n} \quad (1)$$

where ω_n is the resonance frequency. Detailed calculations reported elsewhere [22] show that the \mathbf{q} -dependent prefactor in Eq. (1), also termed the NMR *form factor*, can be expressed as $f_\alpha^2(\mathbf{q}) = M_\alpha + P_\alpha \cos[\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)]$, with M_α and P_α as constants.

The \mathbf{q} -sum in (1) was evaluated numerically using the dynamical susceptibility of an isotropic spin-1/2 Heisenberg chain given by theory [23]. Because of the large exchange coupling ($J = 24.1$ meV $\gg \mu_B B \approx 0.4$ meV), spin chains in $\text{BaCu}_2\text{Si}_2\text{O}_7$ were considered as non-interacting above the ordering temperature and effectively in zero field. Employing the simplest linear description of a Luttinger liquid, i.e., without any scattering of quasiparticles and neglecting the influence of the form factor, the dominant contribution in (1) is at $q = \pi$ and T_1 is temperature independent. It turns out, however, that including $f_\alpha^2(\mathbf{q})$

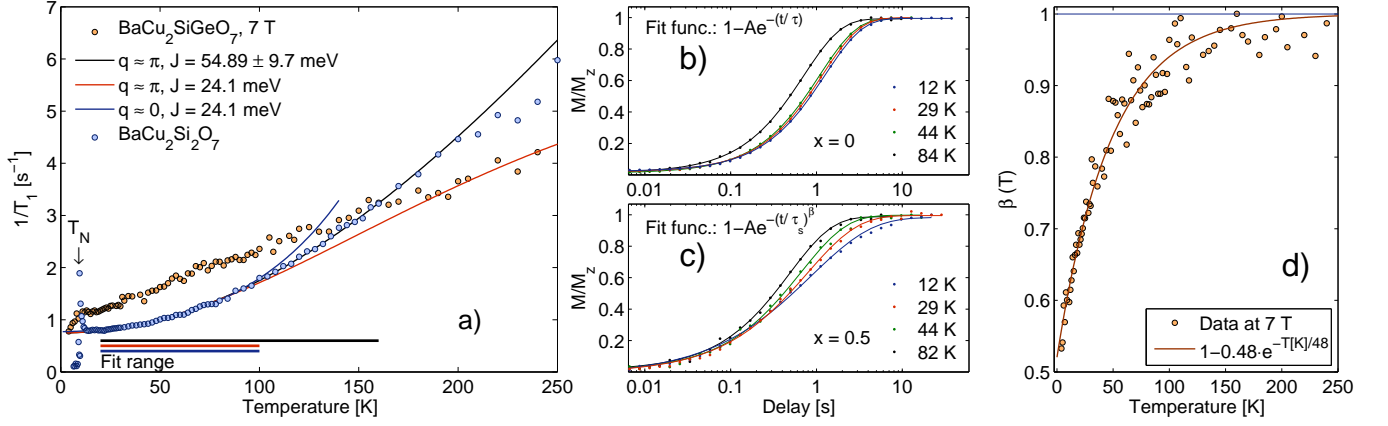


FIG. 3. (Color online) ^{29}Si NMR spin-lattice relaxation data of $\text{BaCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_7$ for $x = 0$ and $x = 0.5$ (no and maximum randomness, respectively). a) relaxation rates for both cases, b), c) recovery of magnetization, and d) T -dependence of β for $x = 0.5$. The symbols are explained in the panels.

is essential to obtain a reasonable fit to the T_1^{-1} data for $x = 0$. Considering $f_\alpha^2(\mathbf{q})$ results in an increase of T_1^{-1} with T , as observed and shown in Fig. 3. A similar increase, without the influence of $f_\alpha^2(\mathbf{q})$, may also be due to a non vanishing scattering of quasiparticles, implying that the dominant contribution is at $q = 0$, as shown in Ref. 24. A convincing demonstration of the different implications of $q = 0$ and $q = \pi$ excitations on the temperature variations of T_1^{-1} was given in Ref. 25 for Sr_2CuO_3 . Additional data of T_1^{-1} with different crystal orientations (not shown here because of space restrictions) confirm that $f_\alpha^2(\mathbf{q})$ cannot be neglected in our case. This fact and the verified absence of significant spin-diffusion effects on the field dependence of T_1^{-1} indicate that the dominant component is at $q = \pi$. In Fig. 3 we display the experimental results together with fits considering the two possibilities mentioned above. Including $f_\alpha^2(\mathbf{q})$ and presuming the zero-field limit, only J , M , and P (the latter two independent of α), are required as free parameters for the fits. The best results are obtained with $J \simeq 55$ meV, distinctly larger than expected. We recall, however, that the evaluation of J via NMR is not straightforward. It enters via a non-zero form factor and its uncertainty depends on the choice of the temperature range of the fit. Nevertheless, the results for the $x = 0$ case show that ^{29}Si NMR clearly probes the Luttinger-liquid physics, hence providing a convenient technique for studying the low-energy excitations also for $x > 0$.

Referring to the latter case, we notice that due to the loss of translational invariance in disordered systems, Eq. (1) is not valid. The translational inequivalence of sites introduces a multitude of *local* nuclear relaxation times. For a nuclear spin $I = 1/2$, the individual relaxations are simply exponential, but collectively they give rise to a system-dependent and generally non-exponential relaxation. If τ is one of the local relaxation times, a possible interpretation for the observed stretched expo-

nential recovery is provided by [26, 27]:

$$\int_0^\infty \rho(\tau, T) e^{-\frac{t}{\tau}} d\tau = e^{-\left[\frac{t}{\tau_s(T)}\right]^{\beta(T)}}. \quad (2)$$

This equation implies that if the same type of relaxation occurs with a probability $\rho(\tau, T)$ and with a characteristic temperature-dependent $\tau(T)$ at different nuclear sites, then the global relaxation function is a stretched exponential, characterized by the parameters $\beta(T)$ and $\tau_s(T)$. Relaxations described by a stretched exponential are quite common in disordered magnets. The temperature dependence of the exponent β has been reported for a number of different systems [28], such as spin glasses, quasicrystals, polymers, etc. In our case, while for $x = 0$ a simple exponential is adequate for describing the magnetization recovery, stretched exponentials are needed for $x = 0.5$. The corresponding data and fits are shown in Fig. 3b and 3c, respectively. From the latter, $\tau_s(T) \equiv T_1$ and $\beta(T)$ are obtained and shown in Figs. 3a and 3d.

Extracting the weights $\rho(\tau, T)$ via an inversion of Eq. (2) is a mathematically non-trivial task [27]. To account for our case, where $\beta \geq 0.5$, we start from Eq. (2), but now using the variable $s = \tau_s/\tau$ [29]:

$$e^{-(t/\tau_s)^\beta} = \int_0^\infty P(s, \beta) e^{-st/\tau_s} ds, \quad (3)$$

where $P(s, \beta)$, as $\rho(\tau)$ before, represents a particular probability distribution function (PDF) of relaxation rates for a given value of β . The inverse of the Laplace transform of (3) [29] provides the required relation between P and ρ , the probability distributions of relaxation rates and times, respectively:

$$\rho\left(\frac{\tau}{\tau_s}, \beta\right) = P\left(\frac{\tau_s}{\tau}, \beta\right) \frac{\tau_s}{\tau^2}. \quad (4)$$

Although $P(s, \beta)$ is obtained only numerically, Eq. (4) allows us to extract the distribution of the local relaxation times in a random Heisenberg chain starting from

the experimental NMR data. Results of this procedure for a series of different temperatures are shown in Fig. 4. At high temperatures, where $\beta \rightarrow 1$, the distribution

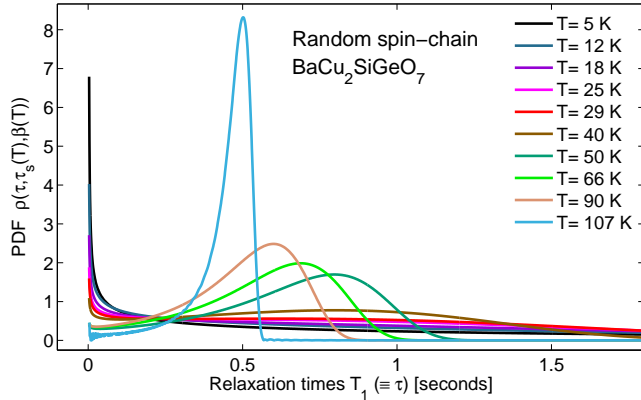


FIG. 4. (Color online) Probability distribution of NMR spin-lattice relaxation times in $\text{BaCu}_2(\text{Si}_{0.5}\text{Ge}_{0.5})_2\text{O}_7$ at different temperatures, as derived from fits to the experimental data partly shown in Fig. 3c.

of relaxation times tends to a delta function peaked at $\tau = \tau_s(T)$, while at low temperatures the distribution diverges weakly as $\tau \rightarrow 0$ and hence remains integrable [27]. In all cases the distribution is normalized and does not depend on temperature, thus reflecting the conserved total number of magnetic sites. In a disordered system the sites are magnetically inequivalent, giving rise to a broadening of the relaxations' distribution at low temperatures. For $T \rightarrow 0$, the distribution $\rho(\tau, \beta)$ peaks at $\tau \rightarrow 0$, but its mean value τ_s increases due to the longer tail of the distribution.

We argue that the measured NMR parameters can be used to obtain information on the low-energy *dynamics* of RHC systems, inaccessible by standard neutron-scattering techniques [16]. In case of randomness, the lack of translational invariance prompts for models based on real- instead of reciprocal-space configurations. In the RS picture, upon lowering the temperature there is an increase in the number of singlets with different couplings being formed, while n_T goes to zero. This results in a continuous distribution of magnetically inequivalent sites and in longer $\tau_s(T)$ at lower temperatures, as reflected in our data. In this low- T scenario the low-energy dynamics is determined by the increasing importance of the “frozen” singlets, at the expense of the yet uncoupled spins. We shall address this point in a forthcoming publication [22].

In conclusion, we have carried out a detailed ^{29}Si NMR study of the spin-lattice relaxation rates in the $\text{BaCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_7$ system for $x = 0$ and $x = 0.5$, corresponding to no and to maximum disorder, respectively. NMR turns out to be an appropriate technique for the study of low-energy dynamics in gapless antiferromagnets

with bond randomness. Guided by the experimental observation that the relaxation of magnetization is characterized by a stretched exponential, we show that it is possible to extract the distribution of relaxation functions in a random Heisenberg chain from experiment. With the additional evidence from magnetization data and QMC calculations, we interpret this result to reflect the formation of random-singlet states in a random Heisenberg chain, as predicted by theory.

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